EXTRACTION KINETICS OF FATTY ACID ETHYL ESTERS (FAEE) FROM OIL PHASE USING AQUEOUS ETHANOL

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ABSTRACT

There is a need for alternative energy sources to replace petroleum based fuels due to the world's crude oil reserves, global warming and environmental concerns. Biodiesel is clean, biodegradable, non-toxic and renewable fuel which is considered to be the best substitution for diesel fuel. In addition, biodiesel has more favourable combustion emission profile, such as low emissions of carbon monoxide, particulate matter and unburned hydrocarbons that make it suitable as alternative fuel in transportation sector. The main issue in biodiesel production is the expensive and non-stable supply of feedstock from vegetable oils. Alternatively, waste cooking oil, tallow and non-edible oils are favourable, although they are restricted feedstock for existing conventional productions of biodiesel due to its impurities such as food residue, biopolymer, cellular remaining, dissolved water and free fatty acids which necessitate additional acidic pre-treatments. The need of extension to the current biodiesel plants resulted in a pursuit of more viable process. One of the potential methods to produce biodiesel from low grade oils and cheap bioethanol is through the extractive reactor. Since, this technique is still new, many physical properties of the oil-alcohol mixture system were not explored. In particular, extraction kinetics of fatty acid ethyl esters from reactive region using aqueous ethanol is essential in order to determine the practicality of the process of extractive reaction for biodiesel synthesis. This experiment was conducted to characterize extraction kinetics of FAEE from oil phase by using aqueous ethanol and to determine the distribution coefficient of FAEE between oil phase and aqueous ethanol. Three different oil:ethanol molar ratio which is 1:1, 1:3 and 3:1 where oil was first diluted with FAEE was used with different stirred time range between 1-20min. A settling time for the mixture was recorded and a sample was taken for concentration determination using gas chromatography (GC) analysis. It is expected that the distribution coefficient of fatty acids ethyl esters (FAEE) is higher in solvent than solution.

Keywords: biodiesel, extraction, aqueous ethanol, cooking oil, FAEE, gas chromatography

ABSTRAK

Terdapat keperluan sumber tenaga alternatif untuk menggantikan bahan api yang berasaskn petroleum berikutan daripada rizab minyak mentah dunia, pemanasan global dan keprihatinan kepada alam sekitar. Biodiesel yang bersih, mesra alam, tidak beracun dan boleh diperbaharui adalah bahan api terbaik utk menggantikan diesel. Selain itu, biodiesel mempunyai profil pelepasan pembakaran yang lebih baik seperti kurang pengeluaran karbon monoksida, habuk, dan hidrokarbon yg tidak terbakar menjadikannya sesuai sebagai alternatif dalam sektor pengankutan. Isu utama dalam pengeluaran biodiesel adalah bekalan bahan mentah daripada minyak sayuran yg mahal dan tidak stabil. Sebagai alternatif, sisa minyak masak, lemak dan minyak yg tidak boleh dimakan boleh digunakan walaupun ianya terhad bagi pengeluaran biodiesel yg sedia ada pada masa kini kerana terdapat bendasing seperti sisa makanan, biopolymer, baki sel, air terlarut, dan asid lemak bebas yang memerlukan rawatan asid tambahan. Keperluan tambahan kepada loji biodiesel yang sedia ada memerlukan lebih usaha untuk memcapai proses yang lebih berdaya maju. Salah satu kaedah yang berpotensi untuk menghasilkan biodiesel daripada minyak gred rendah dah murah adalah melalui reaktor ekstraktif. Memandangkan proses ini masih baru, banyak sifat fizikal system campuran minyak-alkohol belum diterokai. Khususnya, kinetik ekstraktif fatty acids ethyl esters dari kawasan reaktif menggunakan etanol akueus adalah penting untuk menentukan kewajaran proses tindak balas ekstraktif untuk sintesis biodiesel. Eksperimen in dijalankan untuk mencirikan kinetic ekstraktif FAEE dari fasa minyak menggunakan etanol akuos dan untuk menentukan nisbah taburan bagi FAEE diantara fasa minyak masak dah etanol akuos. Tiga nisbah molar minyak:etanol berbeza iaitu 1:1, 1:3 dan 3:1 dimana minyak dicairkan terlebih dahulu dengan FAEE dijalankan dengan berbeza masa dikacau dalam tempoh antara 1-20 minit. Masa campuran untuk setel dicatat dan sampel diambil untuk kepekatan analisis menggunakan analisis gas kromatografi. Dianggarkan bahawa pecahan FAEE lebih banayak di dalam pelarut berbanding larutan.

Kata kunci : biodiesel, ekstraktif, etanol akuos, mintak masak, FAEE, gas kromatografi

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J	Diffusion flow (mass/cm^2.s)
c	concentration of diffusing species (mol/cm^3)
dc/dx	concentration gradient
D	diffusion coefficient (cm^2/s)

Subscripts

δo	thickness of organic films
δw	thickness of aqueous films
R_O	Resistant of organic films
R_W	Resistant of aqueous films
R_i	Interface between organic and aqueous films
V_{nH}	Volume of n-heptane (ml)
V_{EO}	Volume of ethyl oleate (ml)
MW_{nH}	Molecular weight of n-heptane (g/mol)
MW_{EO}	Molecular weight of ethyl oleate (g/mol)
P_{nH}	Density of n-heptane (g/ml)
P_{EO}	Density of ethyl oleate (g/ml)

LIST OF ABBREVIATIONS

FAEE	Fatty acids ethyl esters
GC	Gas chromatography
FID	Flame ionization detector
HLPC	High performance liquid chromatography
KOH	Potassium hydroxide
EtoH	Aqueous ethanol

1 INTRODUCTION

1.0 *Motivation and statement of problem*

Nowadays, the current scenario of biodiesel production is the shortage and unstable cost of feedstock resulting in uncompetitive price of biodiesel. The main problem for current biodiesel production is high cost. According to statistics, 70% of manufacturing cost of biodiesel is from feedstock (Izah et al, 2013). Biofuel feedstock includes many crops that would otherwise be used for human consumption directly or indirectly as well as animal feed. Diverting these crops to biofuels may lead to more land area devoted to agriculture, increased use of polluting inputs resulting in higher prices. Cellulosic feedstock can also compete for resources such as land, water and fertilizer that could otherwise be devoted to food production. As a result, biofuel production may give rise to price and unstable cost of feedstock.

The dominant factor in the production process of biodiesel is the cost of feedstock while capital costs only contribute about 7% (Sani et al, 2013). Therefore, it is essential to utilize cheap feedstock to reduce the overall production cost. Waste cooking oil, animal fat and non-edible oils are potential substitutes and a pre-treatment process using acid catalyst and glycerol extraction was additionally employed in the current plant. There are many works reliable researches, implementation and useful results come to exist. The alternative feedstock must be technically acceptable, economically competitive, environmentally acceptable and easily available. Researches on biodiesel derives from waste cooking oils, animal fats and non-edible oils are being investigated to alternate vegetable oil as biodiesel feedstock.

Furthermore, the utilisation of waste cooking oil is a key component in reducing biodiesel production costs up to 60% until 90% (Kiakalaieh et al, 2013). It is because waste cooking oil is abundantly available in the local market at cheaper rate as it is not commonly used. Meanwhile, a huge quantity of waste cooking oil can be collected from restaurants and food item industry (Shahid et al, 2012). Besides that, biodiesel may also can be produced from less expensive animal fats such as inedible tallow, pork lard and yellow grease (Dhiraj et al, 2012). Animal tallow generated biodiesel offers a wide ranged of energy, environmental and economic advantage (Nelson et al, 2006)

Transesterification is one of the main solutions that have appeared as effective method for using animal fats in diesel engine. Nevertheless, without deep understanding on the equilibrium of liquid mixing during the reaction, transesterification of the low grade oils could not be realistic.

Besides that, a feedstock need a pretreatment process due to its undesired impurities to avoid rection hindrance and saponification problem occurs. Pre-treatment is the first step of biofuel process, and its quality and efficiency of pre-treatment directly affect the subsequent steps. Additionally, pre-treatment is a combination of many process. It consists of a size reduction step followed by chemical, biological or physical treatments (Tong et al, 2013). However,these combinations add extra costs to the production and make the pre-treatment process to become too slow. There are several pre-treatments method that usually used in industries such as steam explosion pre-treatment, dilute acid pre-treatment organosolv pre-treatment, and sulfite pre-treatments (Tong et al, 2013). However, organosolv pre-treatment is limited because of the high operation cost and high cost of organic solvent (Zhao et al, 2009). Tong et al, (2013) from university of Floridahas study a pre-treatment of lignocellulosic biomass for biofuels. He claimed that although pre-treatment is the first step, it is one of the most expensive parts of the entire bioethanol process (Tong et al, 2013)

On the other hand, there is currently a need to improve the commercial feasibility of biodiesel production in order to make it an alternative to conventional biodiesel process. In brief, extractive reaction is one the reactor intensification techniques in order to overcome the reaction hindrance and saponification problems due to undesired impurities in the feedstock. For this purpose, extraction can only be sustained if the medium consistently appears as two-immiscible liquid and the solute is more soluble in the solvent. Hence, this study is essentially to characterize the solubility mechanism and extraction kinetics of fatty acid ethyl esters (FAEE) from reactive region especially at interface by using aqueous ethanol. Briefly, solvent extraction has been defined as a process for transporting materials from one phase to another phase for the purpose of separating one or more compounds from mixtures (Johnson et al, 1983). In the case of biodiesel extraction, FAEE was separated by aqueous ethanol from cooking oil. Aqueous ethanol solution is used as a solvent because of its solubility in water and glycerol that is deposited on lipase surface may be stripped from active active lipasic

sites into the aqueous phase, therefore improving enzyme activity and shifting the reaction equilibrium to the right (Chesterfield et al, 2013)

1.1 *Objectives*

The following are the objectives of this research:

i) To characterize extraction kinetics of FAEE from oil phase by using aqueous ethanol

ii) To determine the distribution coefficient of fatty acids ethyl esters (FAEE) between oil phase and aqueous ethanol

1.2 *Scope of this research*

The following are the scope of this research:

i) Palm oil and ethanol at the ratio of 1:6 at 65^{o}C will be used to extract fatty acids ethyl esters (FAEE) using trans esterification reaction

ii) Ethanol is used as a solvent for this experiment since it is less toxic and more excellent fuel properties compared to methanol

iii) Comparison of the result for different molar ratio of solvent on extractive performance

iv) Analysis of component using gas chromatography

1.3 *Main contribution of this work*

The following are the contributions of this work:

i) Researches on biodiesel for alternative sources of energy to replace petroleum due to environmental concern

ii) Researches on biodiesel derive from low grade oils as alternative to alternate vegetable oil as biodiesel feedstock to reduce biodiesel production cost

iii) Development of integrated process that combine different steps into one single unit through extractive reactor.

iv) Extractive reaction is one the reactor intensification techniques in order to overcome the reaction hindrance and saponification problems due to undesired impurities in the feedstock

1.4 *Organisation of this thesis*

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provides a description about conventional technologies for biodiesel production that implies high production cost due to its operation that need purification of biofuel. This chapter also provides a brief discussion on the integration possibilities for production of biodiesel using waste cooking oil, animal fat and non-edible oil as alternative feedstock to reduce production costs. Besides that, an explanation about the use of aqueous ethanol as a solvent in extraction process is also presented. Futhermore, a general description on rate controlling role of both the chemical reactions and diffusional processes are provided. Lastly, this chapter also explain the principles of solubility and solutions, as well as a summary on previous experimental work on solubilities of various vegetable oils in solvent.

Chapter 3 gives a methodology for preparing calibration curve using GC device approach. Seven samples with different concentration used for concentration determination by FID analysis. This chapter also discuss method for preparation of FAEE. Besides that, brief explanation about methodology to do an experimental study for determination of effect of stirred time on settling time of the mixture and to determine the distribution coefficient of FAEE also presented to give understanding about extraction kinetics of FAEE from reactive region by using solvent aqueous ethanol and solubility mechanism characteristic. Extraction can only be sustained if the medium consistently appears as two-immiscible liquid and the solute is more soluble in the solvent.

Chapter 4 gives result and discussion of this experiment. The result gives an experimental kinetic data refer to a reaction rate and how this is affected by stirrer variables. This chapter also gives an understanding about extraction kinetics of FAEE from reactive region by using aqueous ethanol and solubility mechanism characteristic. It also discusses the extraction kinetics that was controlled by diffusion of FAEE occurring in proximity to the interface with added schematic diagram. Besides that, brief explanation about the distribution concentration of FAEE at both upper layer and bottom layer of mixture of oil:ethanol with different molar ratio also outlined. Lastly, this chapter also explain how different volume of aqueous ethanol will affect the distribution of FAEE in the solution and compare it.

Chapter 5 concluded the whole findings from the experiment process and some recommendation are highlighted when conducting the experiment in order to get better result in future.

2 LITERATURE REVIEW

2.1 *Introduction*

Nowadays, biodiesel that derived from biological sources such as fats and oils have received increasing attention (Dhiraj et al, 2012). Biodiesel can be used to replace petroleum. An intensified search for alternative sources of energy is essential since continuing depletion of the reserves of non-renewable petroleum, price volatility, and feedstock availability concerns (Dhiraj et al, 2002). Besides that, the combustion of petroleum based fuels has causes environmental problems. Thus, it gives impacts on the environment and human health and also threatens wild and human life. Furthermore, the emission of CO, SO_2 and NO_X as the combustion products has cause further global warming. Its part in global warming potential has increased from year by year and now bigger than those of the domestic and industrial sector (Dhiraj et al, 2002).

Biodiesel are most important liquid biofuels in transportation sectors. These biofuels can be uses as a sole fuel in motor engines and as additives in diesel and gasoline blends in other to enhance the oxygen content of such fuel (Gutierrez et al, 2009). These oxygenated blends allow the reduction of polluting gases mostly aromatic hydrocarbons and carbon monoxide (CO) (Gutierrez et al, 2009). In addition, the biodiesel is a mixture of ethyl ester of fatty acids and these ester grouos increases the oxygen content of diesel-biodiesel blend. Therefore, it can improve the combustion efficiencyof conventional follsil diesel (Gutierrez et al, 2009)

2.2 *Conventional technologies for biodiesel production*

Nowadays, the conventional technologies for biodiesel production mostly using a reactor with acid or basic catalyst and separation like distillation, centrifugation, flash evaporation, filtration and decantation that use unit operation (Sanchez, 2010). However, this operation need purification of biofuel that implies high capital investment and energy consumption leading to elevated production cost (Sanchez et al, 2010). One of the important alternative approaches for more intensive and cost effectiveness process is through the development of integrated process that combine different steps into one single unit (Sanchez et al, 2010). Moreover, Gutierrez et al (2009) has been study the integration possibilities for production of biodiesel using a single source of biomass as a feedstock. He claimed that the integration of material flows between

ethanol and biodiesel production lines allowed a reduction unit energy costs down to 3.4%, whereas the material and energy integration leaded to 39.8% decrease of those costs.

Extraction of biodiesel from oil phase using aqueous ethanol is the crucial method in order to imply low capital investment in production of biodiesel. The reactive exraction is an integrated process simultaneous commbining the chemical reaction and liquid-liquid extraction (Sanchez et al, 2010). Briefly, process integration looks for the integration of all operations involve in the production of one specific product. Hence, this can be achieved through the development of integrated processes that combine different steps into one single unit (Sanchez et al, 2010). Besides that, the latter phenomenon allows the continuous removal of the reaction products favouring the direct conversion in the case of reversibel reactions like the esterification of vegetable oils with alcohol. In addition, Sanchez et al (2010), have been evaluating the possibility of applying the integration principle to the biodiesel production by extractive reaction from palm oil. Interestingly, during the esterefication of palm oil with alcohol such as methanol, the product form which is methyl esters ang glycerine generate two immiscible phases. Hence, this will makes the possible to separate removal of two products stream which is biodiesel enriched in extract streams and glycerine enriched in raffinate streams. In this way, the principle of reaction-separation integration can be applied in the production of ethyl esters using palm oil ad even castor oil (Sanchez et al, 2010)

2.3 *Solvent in extraction process*

Aqueous ethanol is used as a solvent in extraction process to produce bioethanol. Fuel ethanol is the most employed liquid biofuel worldwide (Gutierrez et al, 2009). Moreover, a broad variety of plants materials containing the sugars required for fermentation process can be utilized for fuel ethanol production like sugar cane juice and cane or beet molasses. Starchy materials are also used for these purposes (Gutierrez et al, 2009). Besides that, ethanol can be produced from linocellulosic biomass as well. The lignocellulosic biomass is considered as the most promising feedstock at misterm for ethanol production due to its availability and low cost (Gutierrez et al, 2009). In addition, the extraction of palm oil has generates significant amount of lignocellulosic residues which can be used as a feedstock for ethanol production. If the integration of production line for processing both palm oil linocellulosic biomass is considered, hence

the synthesis of an integrated technological scheme for biodiesel is feasible. It is because it will reduce the production cost since there is no need to purchased ethanol because ethanol can be produced within the same process.

2.4 *Solvent extraction kinetics*

The kinetics of solvent extraction is a function of both the various chemical reactions occurring in the system and the rates of diffusion of the various species that control the chemistry of the extraction process (Rydberg et al, 2004)

2.4.1 *Rate-Controlling Role of the Chemical Reactions*

For solvent extraction systems, there are two additional complications. First, the chemical reactions can take place in two bulk phases, since it dealing with two immiscible liquid layers. Second, the chemical reactions can occur in the two-dimensional region called the liquid-liquid interface that separates the two immiscible liquids (Rydberg et al, 2004)

2.4.2 *Rate-Controlling Role of the Diffusional Processes*

In order to understand the dependence of the extraction kinetics on the rate of diffusion of chemical species that participate in the extraction reaction, there is a need to distinguish between diffusion in the bulk phases and diffusion through the thin layers adjacent to the interphase. When two phases are vigorously stirred, it is possible to describe interfacial diffusion by assuming the existence of two stagnant thin layers of finite thickness located on the aqueous and organic side of the interface. This model of interphase is extremely useful for describing extraction kinetics that is controlled by diffusion occurring in proximity to the interface. (Rydberg et al, 2004)

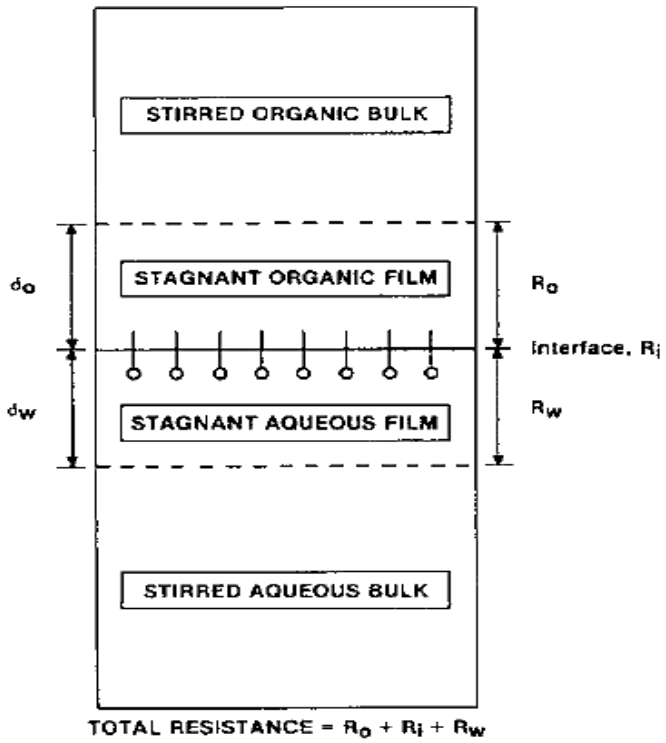

Figure 1 Interfacial diffusion films. (Rydberg et al, 2004)

Figure 1 shows interfacial diffusion films and δ*o* and δ*w* are the thickness of the organic and aqueous films, respectively. The presence of an adsorbed layer of extracting molecules at the interface is also shown in the figure. The thickness of both organic and aqueous films depends on the stirring rate of the two phases. The higher the rate of mixing, the lower the thickness of the diffusion film. In addition, even when dealing with the most efficiently stirred systems, the chemical species that have to be transported to or away from the interface for the extraction reaction to take place always have to diffuse through the diffusion films. The time required for this often can be comparable or longer than that required for the actual chemical changes in the extraction. As a consequence, diffusion through these films controls the overall kinetics of extraction. Experience has shown that film diffusion is the predominating rate-controlling factor in many practical extraction processes. (Rydberg et al, 2004)

2.4.3 *Diffusion*

Diffusion is irreversible process by which matter spontaneously moves from a region of higher concentration to one of lower concentration. Nevertheless, when dealing with solutions containing extractable species (FAEE) and extracting regions at concentrations much lower than those of the molecules of the solvents (aqueous ethanol), diffusion is sufficiently well described by considering only those species for

which the concentrations appreciably change during the extraction reaction(Rydberg et al, 2004)

The diffusion flow, J (mass/cm^2.s) is the amount of matter that passing perpendicularly through a reference surface area during a unit time. When concentration of diffusing species, c are expressed in mol/cm^3, the correlation between the flux across a unit reference area located perpendicularly to the linear coordinate x and the concentration gradient, dc/dx will be given by the Fick's law of diffusion, that is

$$J = - \frac{Ddc}{dx}$$

Where D (cm^2 /s) is the diffusion coefficient of the species and is independent of concentration. (Rydberg et al, 2004)

2.5 *Principles of solubility and solutions*

Solvent extraction is the distribution of solute between two liquids that must not be completely mutually miscible. The distribution of a solute depends on its preference for one or other liquid which is closely related to its solubility in each one of them. Thus, the general subject of solubility is highly relevant to solvent extraction. In solution, the solutes particles interact with solvent molecules and also, provided the concentration of the solute is sufficiently high with other solute particles. These interactions play the major role in the distribution of a solute between the two liquid layers in liquid-liquid distribution systems. (Rydberg et al, 2004)

2.5.1 *Solvent miscibility*

Solvent extraction takes places through the distribution of solutes between two practically immiscible liquids. For a separation to be carried out by solvent extraction, the solute has to transfer from one region of space to another such region, which is physically separated from the first. In phase region, the solute is dissolved uniformly in a liquid at all points under the same pressure. (Rydberg et al, 2004)

2.5.2 *Solubilities in ternary systems*

Ternary systems of interest to solvent extraction are generally two-phase systems, but occasionally ternary systems that consist of a single phase must be considered. It is customary to depict such a system at a given temperature on a triangular phase diagram,

where a composition is indicated by a point in an equilateral triangle. (Rydberg et al, 2004)

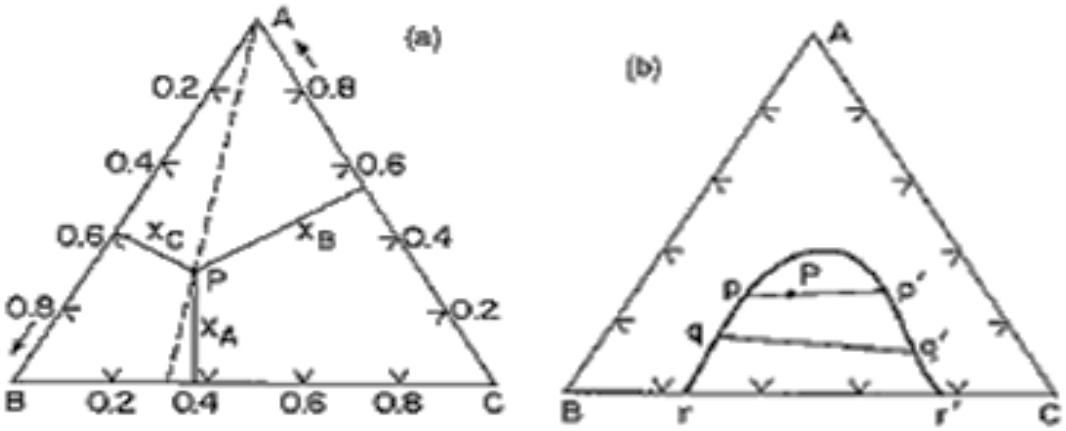

Figure 2 Ternary Phase Diagram with Components A, B And C. (Rydberg et al, 2004)

The figure 2(a) shows a homogeneous system. The composition at point P is being given by the length of the line. This distance represents the corresponding mole fractions. The dashed line shows the changes occurring when solvent A is added (upward) or removed (downward). An apex of the triangle represents a pure component (Rydberg et al, 2004)

The figure 2(b) shows a heterogeneous system, splitting into two liquid phases, with composition market with r, q, p, p', q' and r' along the phase boundary where r and r' denote the BC miscibility gap. A line on the triangular diagram encloses such a region of nominal compositions of the system. A straight tie-line connects the points on the enclosing line that corresponds to phase in mutual equilibrium. At nominal composition P, there is Pp' moles of a phase of composition p for every pP moles of one of composition p', at the two ends of the tie line (Rydberg et al, 2004).

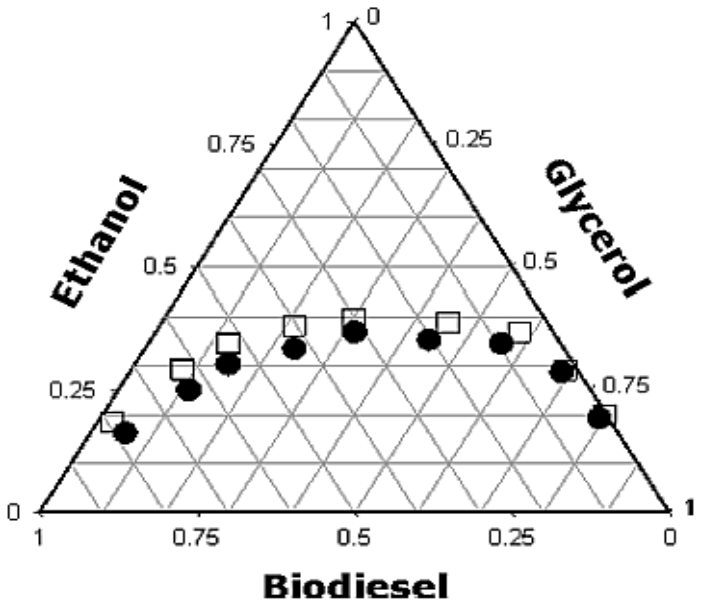

Figure 3 phase diagram of biodiesel + glycerol + ethanol at □ 298.15K and ● 333.15K. (Franca et al, 2009)

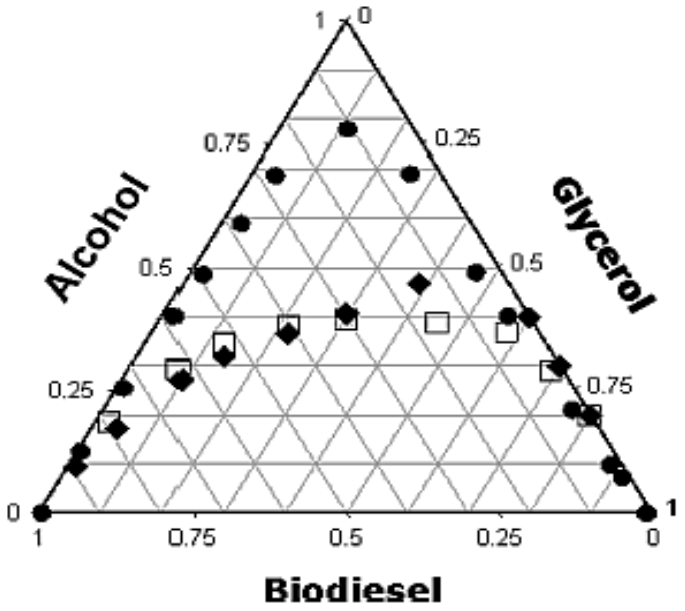

Figure 4: phase diagram of castor oil biodiesel + glycerol + ♦ methanol + □ ethanol at 298.15K. ● Jatropha curcas biodiesel at 298.15K. (Franca et al, 2009)

It can be observed in Figure 3 that biodiesel has greater solubility in the glycerol-enriched phase in the system containing ethanol at 298.15K. Comparing the systems with ethanol at (298.15K and 333.15K) in Figure 4, it can be observed that the solubility increases with temperature. Despite these variations, they are not significant enough to

determine phase behaviour of the systems. The alcohol concentration is the main factor that affects biodiesel product solubility. (Franca et al, 2009)

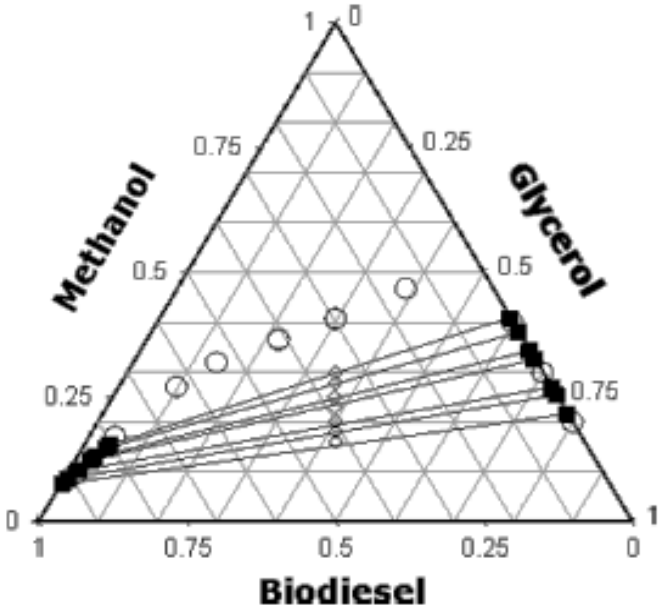

Figure 5 tie lines for the system biodiesel + glycerol + methanol at 298.15K: ○ bimodal; ◇ global composition and ■ tie line. (Franca et al, 2009)

Figure 5 shows the composition of equilibrium phases cross global composition. The solubility of glycerol in the biodiesel phase is slightly greater than that of biodiesel in the glycerol phase. (Franca et al, 2009)

2.5.3 *Solubilities of various vegetable oils in solvent*

From the analysis by Rao et al (1956), the solubility characteristics of babasu oil and coconut oil in ethanol are similar since they have similarity in chemical composition.

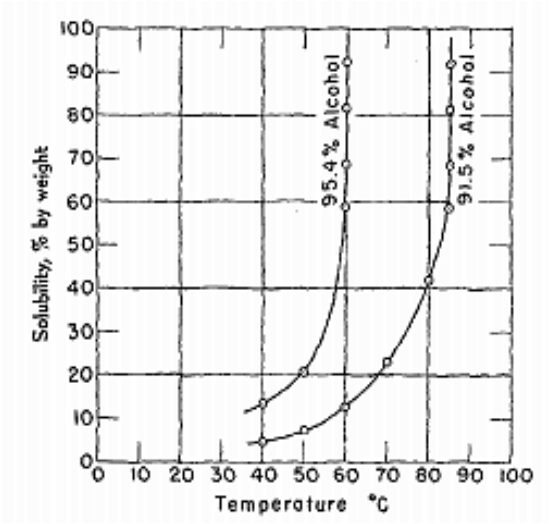

Figure 6 solubility curves for babasu oil (Rao et al, 1956)

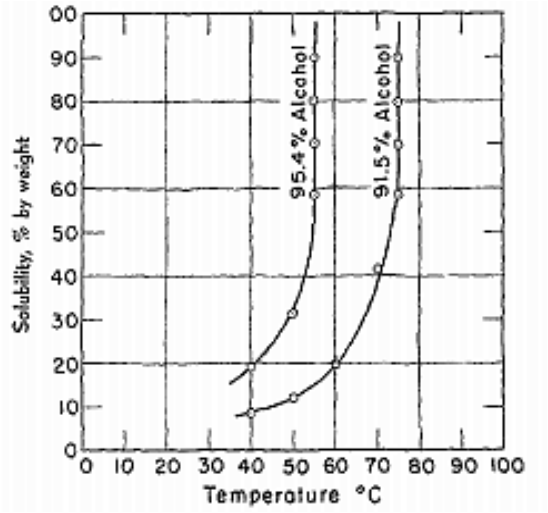

Figure 7 solubility curves for coconut oil (Rao et al, 1956)

Figure 6 shows that babasu oil was miscible in 99.9% ethanol at 30°C while Figure 7 shows that coconut oil was miscible at 23°C. In 98.0% ethanol, miscibility was attained at 45°C for babasu oil and at 35°C for coconut oil. In 95.4% and 91.5% ethanol miscibility temperature were 60°C and 85°C for babasu oil while 55°C and 75°C for coconut oil respectively. The coconut oil was the most soluble of the six oils examined (Rao et al, 1956).

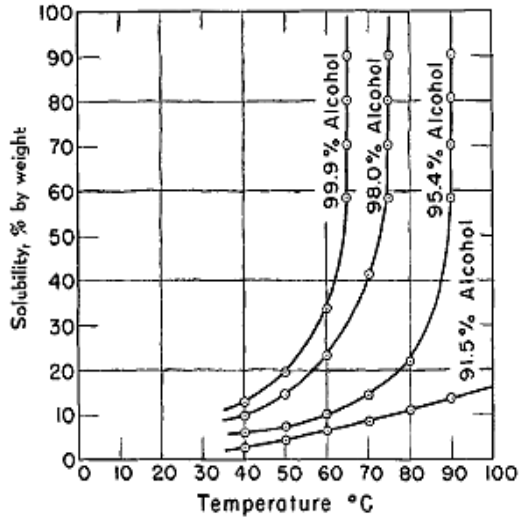

Figure 8 solubility curves for palm oil (Rao et al, 1956)

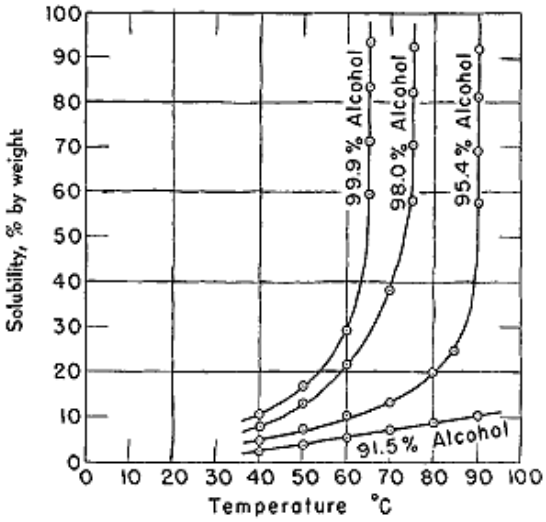

Figure 9 solubility curves for sunflower oil (Rao et al, 1956)

Palm oil (Figure 8) and sunflower seed oil (Figure 9) showed identical miscibility temperature in three highest concentrations of ethanol. In 99.9%, 98.0% and 95.4% of ethanol, the miscibility temperatures was 65^{o}C, 75^{o}C and 90^{o}C respectively. However, in 91.5% ethanol, the solubility of sunflower seed oil was only 10.17% at 90^{O}C compared with 13.5% for palm oil at this temperature. (Rao et al, 1956)

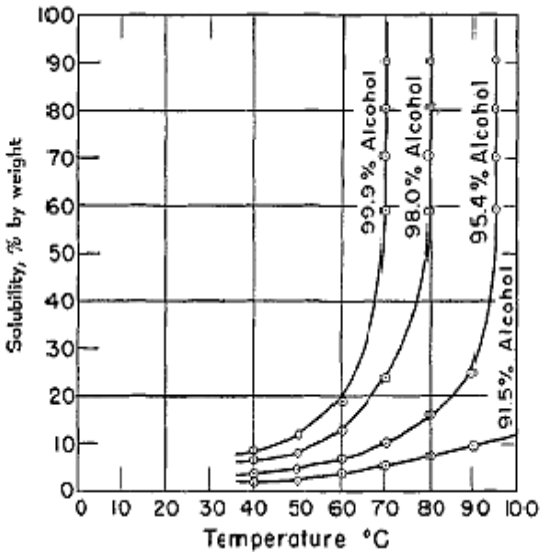

Figure 10 solubility curves for olive oil (Rao et al, 1956)

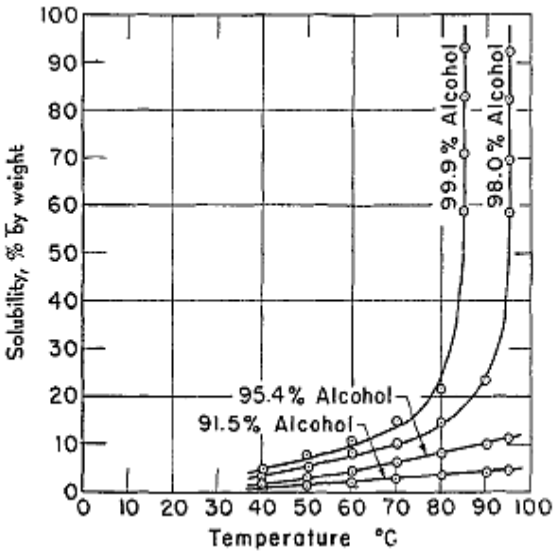

Figure 11 solubility curves for rapeseed oil (Rao et al, 1956)

Figure 10 shows that the miscibility of olive oil in 99.9%, 98.0% and 95.4% ethanol was 70^{o}C, 80^{o}C and 95^{o}C respectively and in each case, it was 5% above palm and sunflower oil. The least soluble of the group was rapeseed oil (Figure 11) with miscibility in 99.9% ethanol at 85^{o}C and in 98.0% ethanol at 95^{o}C. The solubility in 95.4% and 91.5% ethanol at 95^{o}C was only 11.3% and 4.9% respectively. Thus, this oil was the least soluble of the entire group. (Rao et al, 1956)

For overall, it can be seen clearly at 45^{O}C, pure ethanol and oil is partially miscible. We deliberately want to create it to ensure extraction while the dissolve ethanol involve in reaction at low temperature. (Rao et al, 1956)

In addition, from the analysis by Kaparti et al (1959), the saturation solubility of the oils was determined from 40^{O}C to 100^{o}C in 85% by weight to 99% ethanol. It can be seen that the saturation solubility of vegetable oil depends on the concentration and temperature of aqueous ethanol. The solubility are very low at low temperature and